

DILUTE METALS

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Superconductivity (T_c), like any other property of a condensate, depends critically on the concentration of atoms. "Physical" dilution of metals exists in nonstoichiometric compounds. In such stoichiometric compounds as oxides, oxygen initiates "chemical" dilution of the metal, but its efficiency can be estimated only if the real radius of the oxygen ion, $r_0 \sim 0.5\text{\AA}$, is used in the calculation. The ground-state radii of metal atoms $r_m \sim (1.3 - 2.0\text{\AA}) \gg r_0$, so that atoms of metals occupy in the lattice $\sim 90\%$ of the total volume. Therefore, the lattice parameter and the electronic properties are determined by the metal-atom ground states. (For TiO_2 , the parameter $c = 2.95\text{\AA} \sim 2r_{\text{Ti}} = 2.94\text{\AA}$; for TiO , $a\sqrt{2} = 5.99\text{\AA} \sim 4r_{\text{Ti}} = 5.90\text{\AA}$; for BaTiO_3 , $c = 4.05\text{\AA} \sim 2r_{\text{Ba}} = 4.12\text{\AA}$; for Y-Ba-Cu-O , $c = 11.68\text{\AA} \sim (4r_{\text{Ba}} + 2r_{\text{Y}}) = 11.63\text{\AA}$, and so on.) Each atomic quantum state can be identified with a specific physical property of the condensate. As a result of superposition of the ground and ionic states of each metal atom, the fraction of the ground states decreases at the expense of the oxygen-excited ionic ones (thus reducing the effective concentration of atoms). The bands narrow down (in the limit, to the electron localization length), with the metal becoming an insulator, as is the case, for instance, with $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ as x decreases from x_{M} to 0. Conceivably, reducing the lattice deficiency in oxygen by saturating part of its valence bonds with H, Li, or B atoms could increase the T_c ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x} \sim \text{YBa}_2\text{Cu}_3\text{O}_{7-x}(1+x)\text{H}_2\text{O}$). "Self-dilution" of lattices of excited atoms by ground-state atoms was observed to occur in Pd and inert gases.

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I. INTRODUCTION

In describing the properties of oxides, one traditionally assumes the radius of the O^{2-} ion to be 1.4\AA , although about six different figures, ranging from 1.36\AA to 1.76\AA , exists for this quantity. One should therefore treat atoms of metals in oxides as ions with $r_{\text{im}} \sim (0.7 - 0.3)\text{\AA}$, because the interatomic separations constitute ordinarily $(1.7 - 2.2)\text{\AA}$. On the other hand, both quantummechanical calculations [1] and experimental values of the O^{2-} radius (in the O_2 molecule) yield $\sim 0.5\text{\AA}$ (the $2p^6$ state). When using 0.5\AA for the radius of the O^{2-} ion, the sublattices of the metal atoms will be governed by their ground-state radii, which likewise are close to both calculated [1] and experimental values. The ground-state radii of metal atoms, $r_m \sim (1.3 - 2.0)\text{\AA} \gg r_0$, the radii of both the atomic and ionic states of the oxygen atom (0.50\AA), which occupies $\sim 5\% - 7\%$ of the lattice volume. Therefore, the lattice parameters and electronic properties are dominated by sublattices made up of ground-state metal atoms. (For TiO_2 , the parameter $c = 2.95\text{\AA} \sim 2r_{\text{Ti}} = 2.94\text{\AA}$; for TiO , $a\sqrt{2} = 5.99\text{\AA} \sim 4r_{\text{Ti}} = 5.90\text{\AA}$; for BaTiO_3 , $c = 4.05\text{\AA} \sim 2r_{\text{Ba}} = 4.12\text{\AA}$; for Y-Ba-Cu-O , $c = 11.68\text{\AA} \sim (4r_{\text{Ba}} + 2r_{\text{Y}}) = 11.63\text{\AA}$, and so on.)

Adhering to the traditional version (1.4\AA) has not

until recently been critical due to a fortuitous matching of the radii ($r_{\text{O}^{2-}} \sim r_{\text{im}}$). In the case of superconductivity, however, the version of 1.4\AA differs radically from that of 0.5\AA .

A systematic investigation of the properties of condensates in relation to the distances (interaction) among atoms started apparently sometime after 1946, when it was conjectured that dilution of a metal should increase its T_c [2]. In the 1980s, a series of studies of metals diluted by atoms of inert gases (IG) were carried out in connection with the Mott transition (see, e.g., [3, 4]). These investigations did not, however, yield unambiguous results, because "mechanical" dilution of a metal (by ammonia [2] or IG atoms) precipitated it rapidly into a separate phase. As atoms with valence electron pairs are brought close together, the binding energy of the electrons in a pair decreases gradually, and their overlap increases. The possibility of the onset of superconductivity involving localized electronic states in the vicinity of the Mott transition (gas of atoms-the Mott insulator-metal) has long been a subject of debate in its various aspects (see, e.g., [5]). To approach this issue experimentally, one has first to unravel the mechanisms governing the variation of the effective atom concentration in a substance and to learn how to control them properly.

"Physical" (spatial, direct) dilution of metals exists in nonstoichiometric interstitial compounds (nanocomposites, in which, however, metal-insulator-type contact interaction between components exists too).

In oxide-type stoichiometric compounds, "chemical" (indirect) dilution is realized. Each atomic quantum

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state, excited or ionized as well, in a condensate can be identified with a specific physical property. The lattice structure and parameter and the binding energy are determined by the ground and ionic quantum states of atoms. The appearance in the superposition of quantum states of each metal atom of ionic states, which form in the condensate as its atoms interact with oxygen, brings about a decrease in the volume density of ground-state metal atoms (i.e., in the number of such states per unit volume). The latter is equivalent to a decrease of the effective atomic concentration ("chemical" dilution). This gives rise to a band narrowing (in the limit, until complete electron localization obtains), a change in the electron and phonon properties, and to the metal shifting to the insulating state. Such evolution of the properties was observed to occur in $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ as x is reduced from some x_M to 0, i.e., under oxidation of a partially reduced metal in an oxide. An increase in oxygen concentration reduces the volume density of ground states of metal atoms (the effective concentration of atoms) and changes the state of the substance (metal-superconductor-insulator). The potential of increasing (T_c) in this way is limited by the rigid constraints of spatial structures and local inhomogeneity of O^{2-} acceptor distribution for $x > 0$. Uniform increase of the YBaCuO lattice parameter by replacing the O atoms with the larger Se atoms enhanced the dilution of the Y, Ba, Cu sublattice and increased T_c to 371K [6], but at the expense of making the system unstable. A similar effect was observed by substituting smaller atoms (Ag) for part of the metal atoms, although T_c rose to 120K [7].

"Self-dilution" of the same type was found to occur in Pd and IG condensates. In this case, interaction creates excited states, and the lattice of atoms in excited states (i.e., of a larger radius) is diluted by ground-state atoms [8].

II. "PHYSICAL" DILUTION (NONSTOICHIOMETRIC INTERSTITIAL COMPOUNDS)

Metal dilution which does not involve noticeable chemical interactions exists in nonstoichiometric interstitial compounds (nanocomposites). Consider, for instance, MeB_6 [9]. The lattice parameter of the insulator B_6 ($a = 4.15\text{\AA}$) varies depending on the diameter d_m of the metal atom inserted into the B_6 cage. The ratio a/d_m for the metals Ce, La, Ca, Sr, and Ba assumes the following values: 4.15/3.26, 4.15/3.74, 4.15/3.95, 4.19/4.30, and 4.27/4.34. In [9] were taken for d_m the diameters of atoms in the corresponding metals with a packing density of 0.74. The same effect is observed in MeTiO_3 stoichiometric compounds (see below). If Ca in the CaB_6 insulator is replaced by atoms of a trivalent metal, the compounds obtained will be metallic [9]. This justifies the use of metallic diameters. This situation is

shown schematically in Fig.1. The interatomic distances d_m are those of the divalent metal Ca. The packing density of Ca atoms in the B_6 matrix dropped to 0.52, the bands became narrower, and Ca in the simple cubic lattice became a band insulator with effective interatomic separations $d_{\text{mB}_6}^*$. Substituting trivalent metals for Ca results in a half-filled band, with MeB_6 acquiring metallic properties. A similar situation is observed in MeWO_3 tungsten bronzes.

One more aspect of interest is the contact of a lattice of metal atoms with an insulator matrix (the case of metal atoms dispersed in an effective dielectric medium). As is well known from studies of capillary phenomena [10, 11], the metal-insulator contact may give rise to a strong interphase interaction.

Dilution of Na in NH_3 [2] and in WO_3 ($\text{Na}_{0.05}\text{WO}_3$) [12] brought about the onset of superconductivity at about 200 and 90K. In both cases, the systems were extremely unstable, because the superconductivity set in apparently when precipitation of the metal phase passed the stage of formation of Na_2 molecules with a low concentration [13].

III. "SELF-DILUTION" (MONATOMIC CONDENSATES)

Interaction of atoms may result in formation not of ionized but of excited quantum states only. This situation occurs in metallic Pd and in IG condensates [8, 14]. Atoms of Pd and of the IGs have filled electronic shells. The Pd ground-state atom ($4d^{10}5s^0$) has a radius $\sim 0.57\text{\AA}$ [1]. The radius of the atom in the metal, $r_m = 1.376\text{\AA}$, is equal to that of the excited state atom ($4d^95s^1$). While "chemical" dilution gives rise to a superposition of the ground and ionized states, here the atom resides in a superposition of the ground and excited states. The radii of the states are, however, strongly different in this case too. The lattice parameter and the binding energy are determined by the state having the larger radius (the new, excited one). The old (ground) state of a small radius realizes in the form of "quantum cavities and channels", which permit high-rate diffusion, for instance, of hydrogen. The same effect is observed under "chemical" dilution in oxides, but it involves ionic-type states (TiO_2 , see below).

"Self-dilution" occurs in IG condensates too. The state of IG atoms in condensates is also determined by a superposition of the ground ($r_g \sim 0.3 - 0.6\text{\AA}$) and excited ($r_e \sim 1.5 - 2.5\text{\AA}$) states. The only difference from Pd consists in the magnitude of the excitation energy. For Pd atoms, it is ~ 1.3 eV, while for the IG atoms, it is $\sim 10 - 20$ eV. Therefore Pd is a metal in which the effective concentration of excited states is $\sim 75\%$, while that of the ground states ("cavities"), only $\sim 25\%$. For the IG condensates, these states are in the inverse ratio, which makes them insulators, but not of the band type [14]. For instance, the probability of formation in

He of excited states (He^*) governing the binding energy and lattice parameter is $\sim 10^{-3}$. This probability is certainly not high enough even for crystallization of the condensate. Most of the atoms (99.9%) make up essentially a gas of ground-state noninteracting atoms. This figure characterizes the "self-dilution" of He, which is treated by us, however, as a liquid of particles with a radius $\sim 1.5\text{\AA}$, although their number is extremely small. Compression increases their number, and He undergoes solidification.

IG condensates are convenient objects for studying the dependence of the properties of a substance on atomic concentration under compression, including the superconductivity. In monatomic systems (Pd, IG), excited states (*) form in pair interactions. "Virtual" diatomic molecules (condensate as a superposition of the ground and molecular states) are produced. For instance, $(\text{Xe}^*)_2$ is an analog of Cs_2 molecules, which have two paired electrons each. The condensate consists of divalent particles whose concentration depends on the excitation energy and pressure. Their number in Pd is large enough to form a metal, while in He it is too small even to initiate crystallization. Therefore, IG condensates may be considered as strongly diluted, rarefied gases of divalent metal atoms (in the state preceding Mott's transition) embedded in a medium of weakly bound atoms in the ground state (an insulator). In He these are $(\text{He}^{4*})_2$ in a medium of He^4 atoms, or $(\text{He}^{3*})_2$ in a medium of He^3 atoms. The pressure-induced conductivity (or superconductivity) appears initially as a result of formation of a disordered 3D percolation "cobweb" of chains of $(\text{IG}^*)_2$ molecules [8, 14].

IV. "CHEMICAL DILUTION" (STOICHIOMETRIC COMPOUNDS)

"Physical" dilution meets with the problem of stabilization of metal atoms present in a low and uniform concentration. In oxides, oxygen is involved in both the "physical" (spatial) dilution of metal atoms and "chemical". The latter stems from the fact that the diameter of the ionized states (produced in interaction with oxygen) taking part in the superposition of quantum states of metal atoms is much smaller than that of the ground states determining the lattice parameter (volume). This brings about a decrease in the volume density of ground states (in the limit, to their localization), which is equivalent to a decrease of the effective concentration of metal atoms (dilution).

TiO_2 (rutile) may serve as a good illustration. Figure 2 shows a cut of the TiO_2 tetragonal cell in two directions. The radius of the Ti atom $r_{\text{Ti}} = 1.48\text{\AA}$, that of the Ti^{4+} ion, $r_i = 0.48\text{\AA}$, and of the oxygen ion O^{2-} , $r_o \sim 0.55\text{\AA}$ [1]. In the metal, $r_{m\text{Ti}} = 1.46\text{\AA}$. Ti atoms occupy about 95% of atomic volume in the TiO_2 lattice. Therefore, both the lattice parameter and the electronic properties of this oxide are governed

by the sublattice of Ti atoms (in the ground quantum state). The oxygen atoms (acceptors, $\sim 5\%$ of atomic volume) excite ionic-type states, thus reducing the fraction of ground states in the superposition of these Ti atomic states. Interatomic distances in the Ti atom chains (Fig. 2) are the same as in the Ti metal (parameter $c = 2r_{\text{Ti}} = 2.95\text{\AA}$). The decrease of the ground-state concentration in the chains is, however, equivalent to an increase of atomic separations. This brings about a narrowing of the electronic bands and formation of an insulator with a bandgap $\sim 3\text{eV}$ (see Fig. 1). In TiO (Fig. 2), the amount of oxygen is one half that in TiO_2 , and the Ti chains are, accordingly, less diluted (TiO is a semimetal, Fig. 1).

The new, ionic-type quantum states of Ti atoms in TiO_2 , not only have the Ti-O binding energy but give rise to the formation in Ti chains of "quantum cavities", over which, for instance, B or Li can diffuse with a coefficient of $(10^{-3} - 10^{-4})\text{cm}^2/\text{s}$ [15, 16], a figure five to six orders of magnitude higher than those characteristic of conventional solids. In Pd, hydrogen diffuses over small-radius ground-state chains among the excited state atoms [8].

Application of this concept to $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ suggests the existence of a regular 3D network of "dilute" chains of Y and Ba atoms [17]. This 3D conducting network ("gossamer" by [18]) is embedded in a medium of Cu atoms "diluted" by oxygen to the insulator state. As x is varied from x_M to 0, the volume density of ground-state metal atoms (the effective atom concentration) decreases, with the compound crossing the metal-superconductor-insulator stages (Fig. 1). At $x = 0$, the degree of Y and Ba dilution is apparently so high as to make the $\text{YBa}_2\text{Cu}_3\text{O}_8$ lattice close to unstable.

Figure 3 shows cuts of the CaTiO_3 and BaTiO_3 unit cells. As in the case of nonstoichiometric MeB_6 compounds, the Ba atom stretched the perovskite cell from $c = 3.88\text{\AA}$ in CaTiO_3 to $c = 4.12\text{\AA}$ for BaTiO_3 , thus providing a possibility for oxygen ions to displace between the Ti atoms within $\sim 0.2\text{\AA}$. The Ba atom chains are "diluted" by oxygen in the simple cubic cell to the band insulator state (Fig. 1).

V. CONCLUSION

Changing the effective concentration of metal atoms is only one of methods to increase the superconducting transition temperature T_c . It is conceivable that a superconducting state with a high T_c can exist in the vicinity of Mott's transition between the insulator and the metal. Such successive transitions are known to occur in HTSC materials at a change of the oxygen concentration in them, i.e., under variation of the degree of "chemical" dilution of the metal. Such doping is locally inhomogeneous. However, direct methods capable of producing stable systems out of uniformly diluted metal atoms are unknown or still in the stage of

development (for instance, with the use of zeolites as inert diluters [19]). Indirect methods of diluting metals can be properly understood only when using realistic atomic and ionic radii and after establishment of a clear correspondence between the physical properties of condensates and the quantum states of atoms. Does development of superconductors with $T_c > 300K$ appear feasible? Thus far, reports on such substances built only on measurements of the conductivity, with which measurements of the magnetic properties may also be classed ($371K$ [6]). As in [2], the samples were extremely unstable and poorly reproducible. If, however, the above explanations of the reasons accounting for the instability are correct, critical temperatures $T_c > 300K$ may be reachable. To attain uniform "chemical" dilution of metals (as in substitution of Se for O [6]), one would have to use an element with the ionic radius of oxygen but with a valence of $\sim 2(7/8) = 1.75$. Another method is

that of valence bond saturation. This is, for instance, the use of such atoms as H, Li, or B as interstitials. While the system will remain inhomogeneous, the extent of this inhomogeneity may turn out lower than under oxygen deficiency (OH or H_2O in place of an empty O site). In this case, $YBa_2H_{2+x}Cu_3O_8$ will correspond actually to $YBa_2Cu_3O_{7-x}(1+x)(H_2O) \sim YBa_2Cu_3O_{7-x}$. An experimental investigation of the dependence of T_c on interatomic distances (or atomic concentration) would require a quantitative estimation of the extent of the "dilution" of the metal with oxygen. The concentration of divalent particles in pressure-metallized xenon is stable, uniform, and controllable. No magnetic measurements have thus far, however, been carried out [14]. It is known that sulfur and oxygen become superconductors with T_c below $\sim 17K$, but their atoms are paramagnetic.

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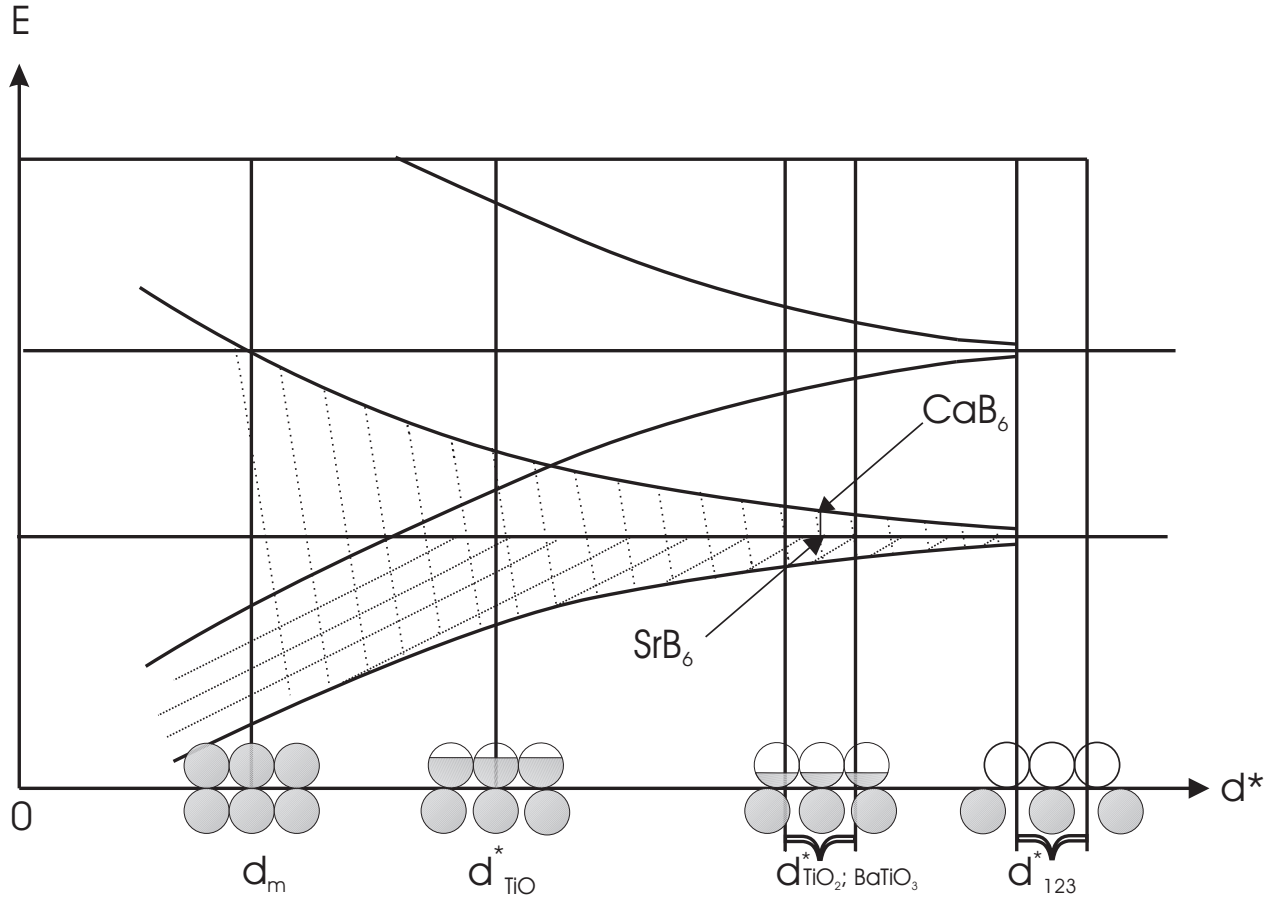


FIG. 1: Schematic of the conceived dependence of states of a substance on the effective distances d^* between metal atoms in an oxide. D_{123}^* varies from $d_{\text{YBa}_2\text{Cu}_3\text{O}_{7-x}}^*$ to $d_{\text{YBa}_2\text{Cu}_3\text{O}_8}^*$.

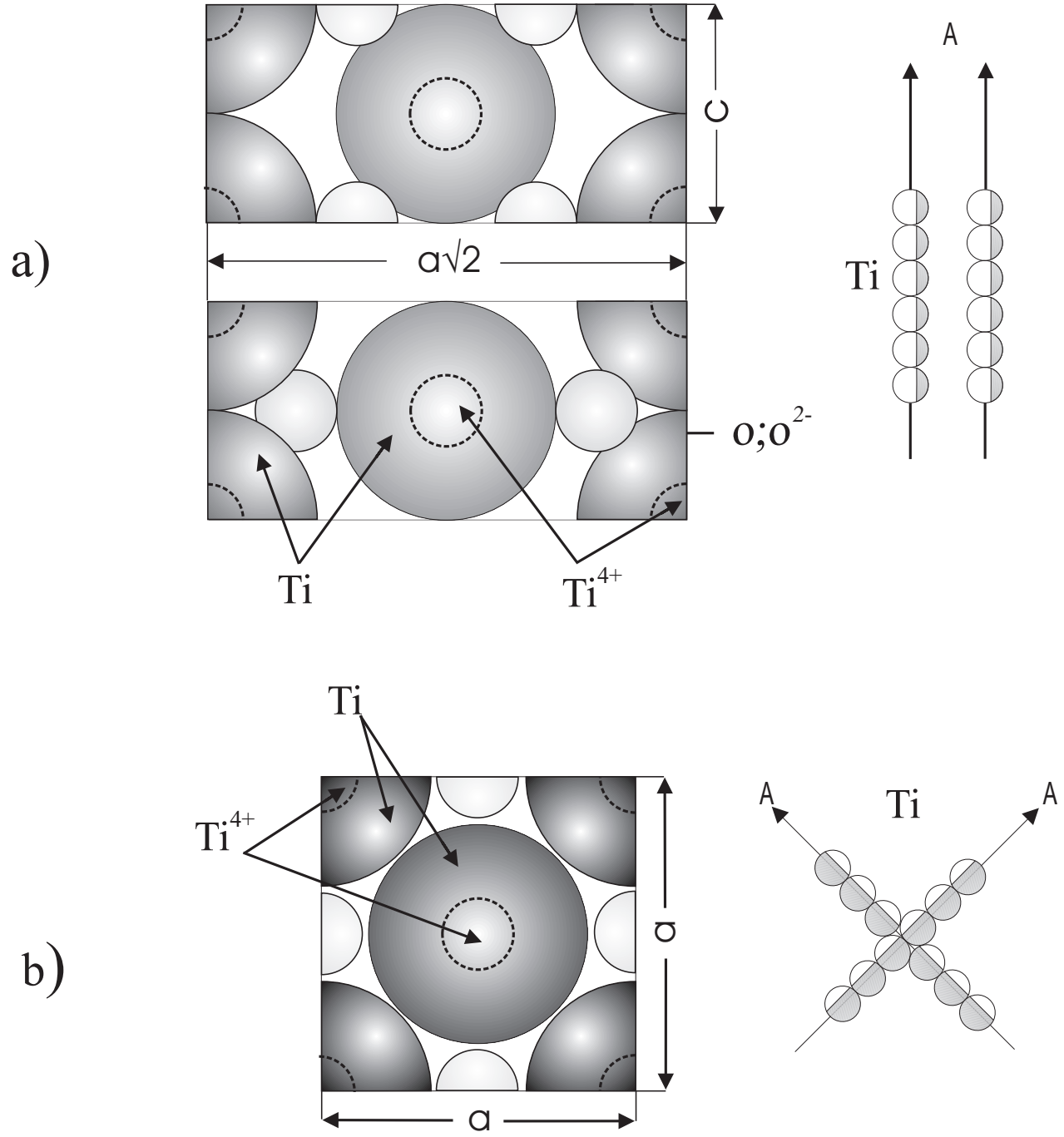


FIG. 2:

(a). Cut of the TiO_2 insulator cell in perpendicular directions; (b) $(a-a)$ face of the TiO semimetal cell. A —direction of the chains of Ti atoms diluted by oxygen.

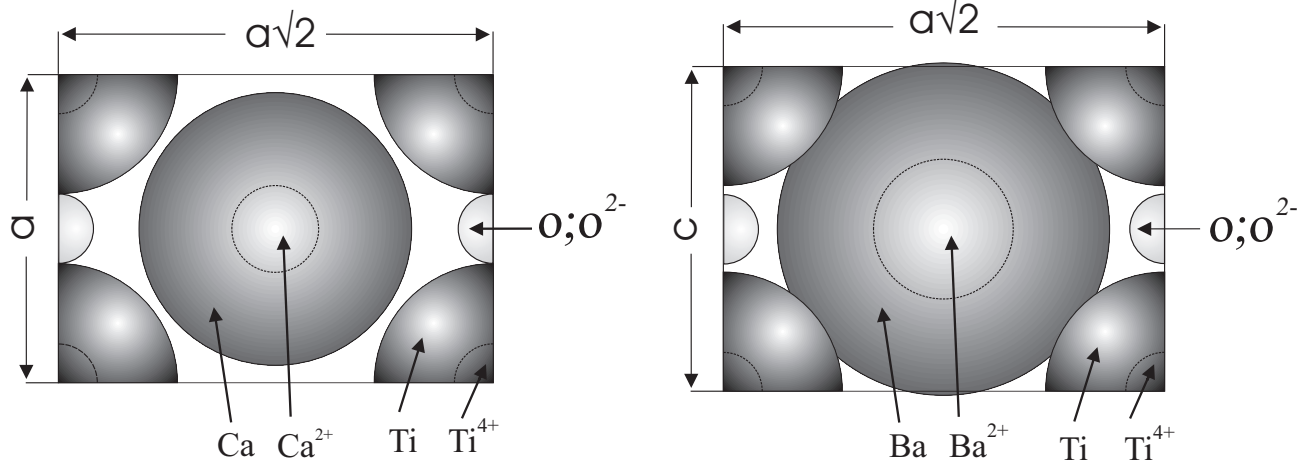


FIG. 3: Cuts of the CaTiO_3 and BaTiO_3 unit cells.